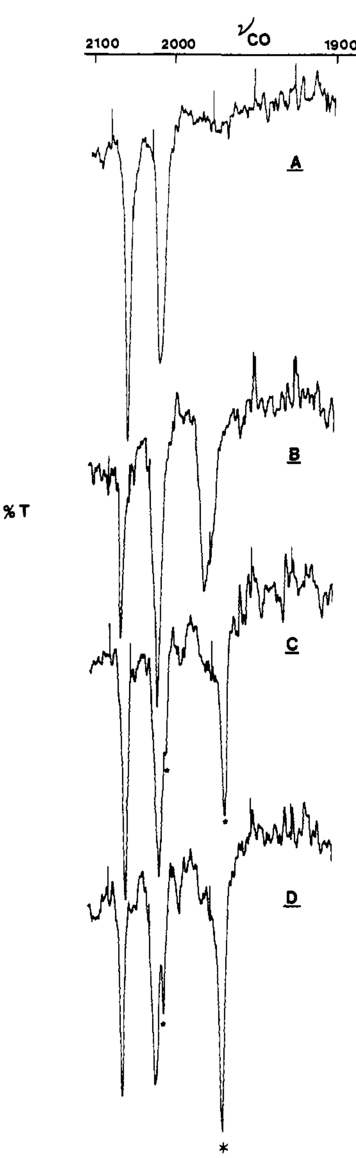


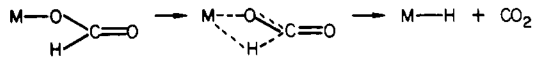
Figure 2. Infrared spectral traces in ν(CO) region of (η^5-C_5H_5)Fe(CO)$_2O_2CH$ in heptane: (A) initial spectrum; (B) after 2 h at 50 °C in ^{13}CO atmosphere; (C) after evacuation of ^{13}CO and admission of ^{12}CO with further heating at 50 °C for 1.2 h; (D) further reaction in ^{12}CO atmosphere for 1 h at 50 °C. Peaks marked by asterisks are due to [(η^5-C_5H_5)Fe(CO)$_2$]$_2$.

carbon monoxide bond lability in low-valent metal carbonyl derivatives containing oxygen donor ligands is emerging as a general phenomenon.[9-12] At longer reaction periods ν(CO) bands are observed which correspond to formation of the [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ species. Simultaneous analysis of the gaseous reaction components by gas chromatography revealed the production of H_2 and CO_2 as well. This decarboxylation process probably proceeds via the (η^5-C_5H_5)Fe(CO)$_2$H intermediate which is unstable under the reaction conditions (eq 5). While reaction

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)Fe(CO)_2H + CO_2 \rightarrow {}^1/_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + {}^1/_2H_2 \quad (5)$$

5 proceeds to completion over several hours at 50 °C, Pettit and co-workers have reported that the metallocarboxylic acid analogue, (η^5-C_5H_5)Fe(CO)$_2$COOH, spontaneously decomposes in solution to [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ plus H_2 and CO_2 at ambient temperature.[4] Therefore, of the two intermediates capable of affording H_2 and CO_2,the metallocarboxylic acid pathway is energetically more favorable.

These experiments unambiguously demonstrate that CO ligand exchange in the (η^5-C_5H_5)Fe(CO)$_2O_2CH$ derivative occurs at a faster rate than decarboxylation. The commonly envisaged mechanism for rupture of the C–H bond in the formate ligand involves the β elimination of a hydrogen atom to the metal center (eq 6).[13,14] Indeed this description would appear to be enhanced



(6)

by the availability of a vacant coordination site on the metal.[15] An added requirement in the (η^5-C_5H_5)Fe(CO)$_2O_2CH$ species, assuming the solid-state structure is retained in solution, is a 180° rotation about the O(3)–C(3) bond in order to achieve the proper rotatomer for β-hydrogen transfer. This effect may not be important in this instance, since rotation about the O(3)–C(3) single bond is expected to be rapid in solution. Although we have not as yet observed the reduction of CO_2 in this system, i.e., the reverse of eq 6, preliminary results on analogous processes in group 6b metal anionic derivatives are in hand (eq 7), where the insertion

$$M\text{-}O_2CH^- \rightleftharpoons M\text{-}H^- + CO_2 \quad (7)$$

of CO_2 into the M–H$^-$ bond is found to be quite rapid.[16]

We are continuing to explore these two reaction processes, namely, dehydrogenation of formate ion in the presence of metals and its retrogradative counterpart, CO_2 insertion into the M–H bond. These reactions are not only of consequence in the homogeneous catalysis of the water-gas shift reaction by metal carbonyls but also in the oxidation of carbon monoxide to carbon dioxide by bacteria.[17]

Acknowledgment. The financial support of this research by the National Science Foundation (Grants CHE 78-01758 and CHE 80-09233) is greatly appreciated.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (2 pages). Ordering information is given on any current masthead page.

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Luminescence and Redox Photochemistry of the Molybdenum(II) Cluster $Mo_6Cl_{14}^{2-}$[1]

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The search for schemes for photochemical energy storage has generated intense interest in the electron-transfer properties of excited states of transition-metal complexes.[2] In the first study of oxidative quenching of a metal complex excited state, tris-

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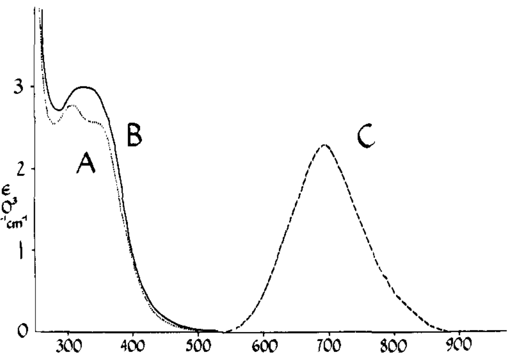


Figure 1. Electronic spectra of $Mo_6Cl_{14}^{2-}$. Absorption, (A) $(NH_4)_2$-Mo_6Cl_{14} in 6 M aqueous HCl; (B) $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN. Emission, C (arbitrary units). The emission spectrum shown is uncorrected; in the corrected spectrum $\lambda_{max} \sim 760$ nm. Similar absorption and emission spectra were observed for solid $(Bu_4N)_2Mo_6Cl_{14}$.

Table I. $Mo_6Cl_{14}^{2-}$ Phosphorescence Lifetimes[a,b]

conditions	300 K	80 K
$(Bu_4N)_2Mo_6Cl_{14}$ solid	120	210
CH_3CN soln	180	c
$(H_3O)_2Mo_6Cl_{14}$ in aq 6 M HCl, 6 M LiCl	20	80

[a] ±10%. [b] In μs. [c] Not measured.

(2,2′-bipyridine)ruthenium(2+), or $Ru(bpy)_3^{2+}$, was used as the photoreceptor.[3] Since then, in addition to a number of thorough investigations of $Ru(bpy)_3^{2+}$,[4,5] other complexes, such as $Cr(bpy)_3^{3+}$,[6] *fac*-$Cl(CO)_3Re(1,10\text{-phen})$,[7] and Rh_2(diisocyanoalkane)$_4^{2+}$,[8] and certain porphyrins[9] and phthalocyanines[10] have been shown to exhibit similar behavior. In all of these complexes, however, the organic ligands interact strongly with the metal atoms and are heavily involved in the long-lived excited states. We now report the phosphorescence of the octa-μ_3-chloro-hexachlorohexamolybdate(2−) ion, $Mo_6Cl_{14}^{2-}$, and simple electron-transfer reactions in its ground and excited states. The durability of this all-inorganic ion in solution and its capacity for efficient absorption of visible light make it particularly attractive for experiments in solar energy storage.

The general $[M_6X_8]L_6$ cluster structure occurs in a number of compounds with M = Mo or W, X = halide or alkoxide, and L = various donors. The axial ligands L are easily replaced in protic solvents and the bridging ligands X undergo substitution under more vigorous conditions (such as in refluxing basic solution or in molten salts), but the octahedral M_6 core is unaffected. Figure 1 shows absorption and emission spectra for $Mo_6Cl_{14}^{2-}$ in acetonitrile and aqueous HCl solutions at room temperature. The emission spectra are essentially identical for the two solutions ($\lambda_{max} \sim 760$ nm), but they differ in intensity: estimated lower limits for emission quantum yields, by comparison with $Ru(bpy)_3^{2+}$,[11] are 0.04 and 0.005 for the acetonitrile and hydrochloric acid solutions, respectively. Absorption spectra recorded for single crystals of $(Bu_4N)_2Mo_6Cl_{14}$ at low temperature (~30 K) reveal weak shoulders at 530 and 590 nm. It is likely that the 590-nm absorption is associated with the luminescent excited state.

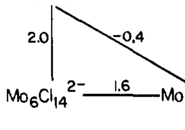
The phosphorescence lifetimes in Table I, obtained from emission decay kinetics under 337-nm illumination from a pulsed nitrogen laser, are among the longest known for any transition-metal complex. That the lifetime is substantially shorter in aqueous HCl than in CH_3CN is in rough agreement with the observed change in emission quantum yield. We have also observed a transient absorption signal between 450 and 600 nm in a flash kinetic spectroscopic study of an acetonitrile solution of $(Bu_4N)_2Mo_6Cl_{14}$. Because this signal decays exponentially with a lifetime comparable to that observed in emission, we attribute it to the phosphorescent excited state, $Mo_6Cl_{14}^{2-*}$. We have also observed luminescence in acetonitrile solutions of $(Bu_4N)_2Mo_6Br_{14}$ and $(Bu_4N)_2W_6Cl_{14}$; the corrected emission maxima are 775 and 825 nm, respectively. The close similarity of the $Mo_6Cl_{14}^{2-}$ and $Mo_6Br_{14}^{2-}$ emission spectra indicates that the electronic transition from the phosphorescent excited state to the ground state is primarily localized in the $[Mo(II)]_6$ core of the cluster anion.

Although reversible redox reactions are well documented for the related $(Nb,Ta)_6X_{12}$ species, attempts to oxidize or reduce the Mo and W clusters in a similar fashion have generally been unsuccessful. Bromine oxidizes $[W_6Br_8]Br_4$ to derivatives of $W_6Br_8^{6+}$,[12] and the $[M_6Cl_8]Cl_4$ species are oxidized under more vigorous conditions to new clusters with the $[M_6Cl_{12}]$ core structure.[13] Various phosphines have been shown to reduce $Mo_6Cl_8^{4+}$-containing compounds to complexes of the type $[(Mo_6Cl_8)(PR_3)_6]^{2+}$.[14] More recently, Gibson and Meier have found evidence for disproportionation by intermolecular electron transfer in EPR spectra of γ-irradiated solid $[Mo_6Cl_8]Cl_4$.[15] Our electrochemical experiments, however, provide the first evidence that clusters of this type can undergo simple electron-transfer reactions in solution: cyclic voltammetry performed on $(Bu_4N)_2Mo_6Cl_{14}$ in acetonitrile reveals a nearly reversible, diffusion controlled one-electron oxidation wave at 1.29 V vs. Ag/0.1 M $AgNO_3$. The fact that this oxidation wave appears at a potential that is about 0.6 V more positive than that for Cl^- confirms that the chloride ligands in $Mo_6Cl_{14}^{2-}$ are firmly bound.

The combination of luminescence and redox properties of $Mo_6Cl_{14}^{2-}$ led us to investigate the effects of added electron acceptors. Initial experiments showed that methyl viologen (1,1′-dimethyl-4,4′-bipyridinium or MV^{2+}), quenches the luminescence of $Mo_6Cl_{14}^{2-}$. Transient absorption attributable to MV^+ is observed in flash kinetic spectroscopic studies of solutions containing both ions. Thus we conclude that quenching proceeds by electron transfer from $Mo_6Cl_{14}^{2-*}$ for a general electron acceptor A.[16]

$$Mo_6Cl_{14}^{2-*} + A \rightarrow Mo_6Cl_{14}^- + A^-$$

These quenching experiments combined with the electrochemical data lead to the following diagram (excited state energy in eV; electrode potentials estimated vs. SCE in CH_3CN).



The cluster ion $Mo_6Cl_{14}^{2-}$, as a representative of the lower halides of Mo and W, offers attractive features for photochemical studies: its excited state is long lived and of relatively high energy, and the $Mo_6Cl_{14}^-$ ion, readily produced by electron-transfer quenching, is a powerful oxidant. We are currently examining photoredox reactions of $Mo_6Cl_{14}^{2-}$ in aqueous solution. Here the

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spectral and redox properties of the $XW_{12}O_{40}$-type heteropolytungstates[17,18] appear ideal for oxidative quenching. We are also studying the photochemical properties of the related $Mo_6Br_{14}^{2-}$ and $W_6Cl_{14}^{2-}$ ions.

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Eigenfunctions of Open-Shell Molecules: Experimental Spin Densities in CrF_6^{3-} and $CoCl_4^{2-}$

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Diffraction of X-rays, electrons, and neutrons by crystals offers the only direct relationship between observations (Bragg intensities) and the wave function sampling, for example, Fourier components of the electron density or, in the case of polarized neutron scattering, the magnetization density. The magnetization density is due to both the intrinsic magnetic moment of electrons (spin) and the magnetic moment generated by "moving" electrons (orbital magnetization). Since in the CrF_6^{3-} and the $CoCl_4^{2-}$ ions we have orbitally nondegenerate ground states ($^4A_{2g}$ and $^4A_2$, respectively), one can associate the magnetization density very largely with the appropriate one-electron spin density distributions. The spin distribution may be expressed in terms of the partial occupation of molecular orbitals, perhaps accompanied by some polarization of fully occupied orbitals.

Crystals of K_2NaCrF_6 were examined by Wedgwood:[1] polarized neutron scattering by the cubic crystals, held at 4.2 K and placed in a strong magnetic field, was analyzed to discuss spin transfer from the chromium(III) ion to the fluoride ions and the covalence in the Cr–F bonds associated with the transfer. Wedgwood's theoretical analysis was limited to Fourier methods which have well-known disadvantages.

The $CoCl_4^{2-}$ ions in crystals of Cs_3CoCl_5 have been examined even more fully,[2,3] and the crystallography is particularly advantageous in so far as a number of observed magnetic reflexions have intensities due to ligand effects alone; covalence can thus be measured rather more directly.

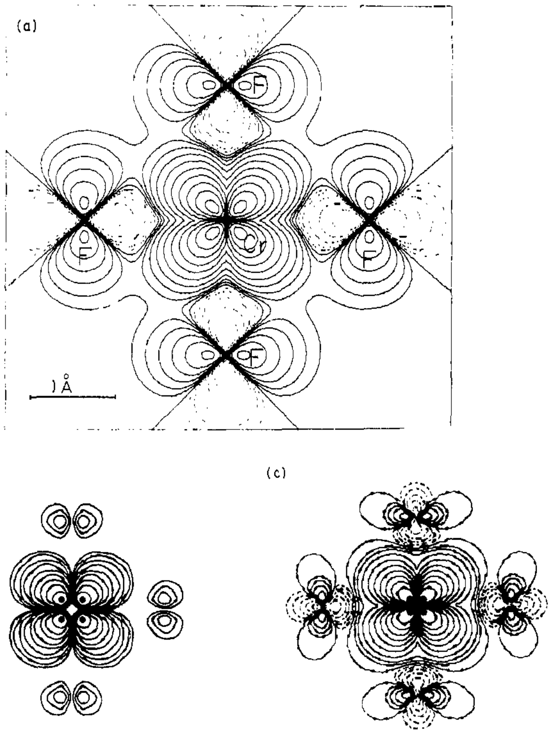

Figure 1. Sections of the residual spin density of the octahedral CrF_6^{3-} ion determined from (a) a multipole analysis[4] of the magnetic structure factors of K_2NaCrF_6 measured by Wedgwood,[1] (b) a restricted Hartree–Fock calculation, and (c) an unrestricted Hartree–Fock calculation by using a double zeta basis. The first continuous contour represents zero spin density. The *n*th contour from the zero contour represents the $\pm 2^{n-1} \times 10^{-3}$ e/Å^3 density contour. The dotted contours represent negative spin density.

We summarize a model which provides experimental spin densities in such a way that it allows immediate comparison with theories of valence. The one-electron density in the unit cell is expressed as a superposition of one-center density functions expanded as a linear sum of density fragments of the type[4]

$$\rho_{lm}(r,\theta,\phi) = M_l^m N_l^m Z_l^m(r,\theta,\phi) R_l(r)/4\pi$$

$$(l = 0, 1, 2, ..., -l \le m \le l)$$

with *M*, *N*, and *Z* being, respectively multipole populations, normalization factors, and Tesseral harmonics; *R*(*r*) is the radial wave function for the appropriate center. Symmetry often significantly restricts the number of nonzero multipoles, but, more generally, the multipole populations and the radial exponents are well determined by a least-squares fitting procedure to the observed magnetic structure factors, with the structure factor being recast into the form

$$F_{\text{calcd}}(\mathbf{S}) = \sum_{\text{cell}}\left(\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l M_{j,l}{}^m N_l{}^m 4\pi \langle \mathcal{J}_{j,l} \rangle Z_l{}^m(\alpha,\beta) \exp[-i2\pi \mathbf{h}\cdot\mathbf{x}_j - \mathbf{h}^t\cdot\boldsymbol{\beta}_j\cdot\mathbf{h}]\right) \tag{1}$$

$\mathcal{J}_l$ are spherical Bessel functions; $\mathbf{h} = (\bar{h},\bar{k},\bar{l})$ are *Miller* indexes listed with respect to the reciprocal lattice cell edges *a**, *b**, *c**; $\mathbf{x}_j$ and $\boldsymbol{\beta}_j$ are the positional coordinates and mean-square displacement tensor of the center *j*.

While we have shown[4] that the multipole populations can often be interpreted in terms of "orbital" populations, we demonstrate here the value of constructing the spin density by the superposition of the density fragments within a sphere containing the complex ion. We need the expression

$$\rho(\mathbf{r}) = \sum_{\substack{\text{sphere}\\ \text{centers } j}} \sum_{lm} \rho_{lm}{}^j(\mathbf{r} - \mathbf{r}_j) \tag{2}$$

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